Abstract No. maro335

Biological Metal Clusters: Biophysical and Model Studies

M. Maroney (U. Of Massachusetts), A. Klein, R. Bingemann (FB Biologie Molekulargenetik), B. Friedrich, T. Burgdorf (Institut fur Biologie), F. Al-Mjeni, P. Carrington, P. Bryngelson (U. Of Massachusetts) and S. Albracht (U. Of Amsterdam)

Beamline(s): X9B

ABSTRACT: Ni K-edge XAS is being used to examine the structure of the Ni-Fe heterodinuclear active site in various forms of the enzyme hydrogenase that are related by redox poise and the presence of inhibitors. In collaboration with the Marburg group, we have collected data on the NiFeSe enzyme, where one of the Ni cysteinate ligands in the active site is replaced by selsnocysteine, and are analyzing the both Ni and Se K-edge spectra in order to monitor metal-centered and ligand-centered chemistry. In collaboration with the Berlin group we anticipate collecting data on *Ralstonia eutropha* hydrogenase samples that are well characterized with respect to their redox poise and the presence or absence of NAD(H). This study is important because data reported by us (and others) earlier on fully oxidized and fully reduced enzyme show a structural change in the Ni site upon reduction that is not observed in hydrogenases from other sources. FTIR studies show an extra group in the triply bonded region that has been interpreted as a Ni-CN group that is not present in other enzymes as well. Such a group has not been seen by XAS to date. Last, it is now possible to examine the structure of the epr-silent active hydrogenase from *Chromatium vinosum.* In collaboration with the Amsterdam group we will examine this form and compare it with the structures of the other 11 states of this enzyme that we have examined.